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CONTROLLED MICROSTRUCTURE OF REFRACTORY BODIES

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Introduction

The development of controlled microstructures is currently the dominant theme of the producers of refractory ceramics. The characterization of the microstructure in a refractory body has been the most difficult problem for those engaged in studying the mechanical properties of such systems. The extensive studies on the mechanical properties of polycrystalline ceramics[1] have revealed the necessity of achieving controlled and reproducible microstructures to attain the degree of reliability required by designers of engineering structures for high temperature service. Although the mechanical properties of polycrystalline refractory bodies are currently of greatest interest, other physical properties and the chemical properties are influenced by the microstructure. In the further development of ceramics as engineering materials the relationship of these properties to the microstructure will become increasingly important.

Microstructure of Refractory Materials

The microstructure of a material in its most restricted usage implies the observation and information gained by use of the microscope. The developments in equipment and extension of techniques for sample preparation have increased the utilization of both the optical and electron microscopes. These two tools can be used to describe the size, shape, and distribution of crystalline compounds in a ceramic body. Further, the presence and relative amount of other crystalline phases, glassy phases, and porosity may be determined. Analysis of photomicrographs can also be used to determine the relative grain boundary contact area of one crystal species in a multiphase body.[2]

The observed microstructure, however, is only the starting point when the microstructure must be characterized as to its effect on physical and chemical properties. The interface developed between adjacent grains or between two phases will be the most important microstructural feature. In metallic systems the grain boundary energy has been calculated for pure tilt boundaries and combination tilt and rotation boundaries from basic dislocation theory. Further calculations based on the energetics of crack formation at a boundary indicate that for metals the grain boundary weakening will be relatively small.[3] For ionic or covalent crystals where short-range bonds between individual pairs of atoms are important, high angle boundaries may be expected to be weak. The implications of the arguments

for weakening at grain boundaries in refractory bodies have prompted Gilman[3] to state that grain boundary weakness is an intrinsic characteristic of refractory nonmetallic substances.

The difficulties in forming dense single-phase refractory bodies have led to the use of aids for densification and grain size control. These controlled additions although present in amounts generally under two percent may and quite probably do have a marked influence on the properties of the processed material. Further, the production of many ceramic bodies useful at elevated temperatures is based on forming a liquid phase during the heat treatment. This liquid phase may be retained as a glass at room temperature or itself nucleate and precipitate other crystalline phases in a complex glass-crystal matrix.

The ideal characterization of a microstructure in a refractory body should include:

(1) The size, shape, and distribution of all the crystalline compounds making up the refractory body. The distribution of the phase implies whether or not the phase is continuous or exists as isolated particles in a continuous matrix.

(2) The size, shape, distribution, and orientation of porosity present in the body. This includes both intragranular porosity and that porosity associated with grain boundaries or found in dispersed or continuous minor phases.

(3) The amount and distribution of glass present in the body.

(4) The chemical composition of all associated phases and the degree of concentration gradients established in individual grains or phases.

(5) The strains imposed on the bulk shape due to processing and the microstrains imposed on individual grains due to crystal anisotropy or the presence of secondary phases.

(6) The nature of developed interfaces between crystals of the same species or between phases in the body. Whether or not these interfaces can support tensile or shearing stresses.

It is readily apparent that the microscope alone cannot give the information needed to fully characterize the microstructure. Other tools and techniques are needed. Some are available; however, the most important area, that of the interface, cannot be directly attacked in polycrystalline materials.

The Development of Polycrystalline Single-Phase Bodies

The ideal microstructure proposed by Parker[4] for a refractory ceramic body is one fully dense and of grain size small enough to prevent the formation of the number of dislocations necessary to nucleate a crack

by piling up at a surface or grain boundary. This hypothesis and the extensive experimental evidence[1] on the effect of porosity and grain size have challenged the processer to provide such a microstructure. Investigations on processing oxides, nitrides, carbides, beryllides, and borides into dense fine-grained shapes have covered an exhaustive number of processing schemes. Two primary methods, however, are most frequently used. The first is a method of precompaction of a refractory powder followed by a sintering operation, and the second involves the simultaneous application of heat and pressure to a refractory powder.

In the first method the precompaction of refractory powders may be accomplished by pressing, extrusion, slip casting, or more recently isostatic (hydrostatic) pressing. The precompaction step may achieve densities as high as 85 percent of the theoretical density or as low as 30 percent. The exact nature of the powder's response to the precompaction operation depends on the character of the powder and is one of the most least understood areas of ceramic processing. The particle shape, size, size distribution, surface activity, degree of chemical purity, etc., are all parameters in determining the material's response to the forming method.

The sintering operation following precompaction is on a firmer scientific basis. The accepted mechanism for densification by sintering of most refractory compounds is that of volume diffusion.[5] The driving force for densification, the crystal surface energy, creates two major barriers to achieving a fine-grained microstructure. First, grain growth can also reduce the total energy of the system by reducing grain boundary area, and second, erratic growth of individual grains (discontinuous grain growth) may occur. Achievement of high density and fine grain size together has rarely been made in the oxides where most investigations have been concentrated. Recent investigations[8] on alumina, however, have developed a method of sintering using a sintering aid and atmosphere control to achieve a dense translucent body with grain size control. The translucent character is probably a better criterion for the elimination of porosity than any bulk density method or microstructural technique.

The effect of atmosphere control to prevent insoluble gases from being trapped in pores allowed the densification process to proceed by volume diffusion. The addition of less than two percent magnesia to the body controlled the rate of grain growth and prevented discontinuous grain growth. The virtual elimination of porosity and the controlled grain size have allowed more quantitative evaluation of the effect of microstructure on mechanical properties; however, even in this process difficulty is experienced in attaining grain sizes on the order of one micron without some residual porosity. The normal grain size for the translucent material is about ten microns or above.

By using controlled decomposition of hydroxides or other compounds, a sinterable magnesia or beryllia powder can be produced.[9] These powders will sinter to densities approaching the translucent state, but grain size control is even more difficult than in the case of alumina.

The results of sintering as a method of achieving high density and fine grain size in other refractory compounds have been less successful.

Sintering aids such as titanium dioxide added to uranium dioxide or calcium oxide added to thorium oxide have promoted increased densities but have not been investigated thoroughly enough to predict in advance a density-grain size combination attainable.

Hot pressing of refractory compounds has received considerable attention.[6] The short times that the material is held at the elevated temperatures reduce the grain growth. The addition of pressure at temperature accelerates the densification process. Through the use of an aid to hot pressing, magnesium oxide and beryllium oxide have been hot pressed to translucency. In magnesium oxide[10] a lithium fluoride addition (under two percent) is added to the magnesia powder prior to hot pressing. After hot pressing a heat treatment in air or vacuum is required to eliminate the fluoride addition and to develop translucency.

The exact mechanism of densification during hot pressing is still being debated. It is probably safe to predict that hot pressing involves two and possible three mechanisms. Particle sliding during the early stages,[11] a pressure-accelerated plastic deformation by a Nabarro-Herring type diffusion mechanism, and normal volume diffusion all may be involved. The addition of hot pressing aids probably promotes a liquid phase and extends the complexity of the mechanisms involved.

The properties of hot pressed and sintered refractory bodies have not been compared for the same grain size, porosity, chemical purity, etc. Consequently, the microstructure developed by the two techniques has not been compared but individually analyzed. To date, microstructural details such as the average grain size and size distribution, porosity location, distribution, and evidence of preferred porosity orientation due to processing have not been reported. These details must be forthcoming if the microstructure can be characterized as being controlled.

Direct melting and casting of refractory compounds has not been successful in producing bodies with desired microstructures, except in the case of uranium monocarbide. Large grain sizes developed in the few materials attempted in the oxides have given bodies so weak that normal stresses developed in cooling cause cracking of the shape. Other methods of forming are still in primitive states of development and their applicability to produce controlled microstructures is impossible to assess.

The Development of Multiphase Bodies

The methods of producing a multiphase refractory body include those for single-phase bodies and several novel approaches. Typical bodies in such systems contain a refractory crystalline phase with secondary crystalline phases of a metallic or inorganic nonmetallic character or a glass. The glass-crystal combination is the system most frequently encountered in refractory bodies. The production of such a system may be unintentional in attempting to produce a dense polycrystalline single-phase body due to uncontrolled impurities present in the refractory powder. However, most systems are intentionally compounded with controlled additives added to promote the formation of a liquid phase during sintering.[7] The resultant body is

an intimate association of a glass phase, crystalline phase or phases, and usually closed porosity. The amount and distribution of the glass phase is extremely difficult to determine at low volume percentages and small grain sizes of the crystalline phase. Commercial high alumina bodies with alumina contents varying between 95 and 98 percent are examples of this type of system. Because of the lack of tools and techniques to quantitatively determine the composition and amount of glass present in such systems, microscopic examination is used to determine the amount and distribution of the glass. The composition and amount of the glass phase also can be estimated from the phase equilibrium diagram for the system if available and with a prior knowledge of the thermal treatment. At the best these data are qualitative due to unknown reaction kinetics.

The interface in such systems is extremely complex. Few wetting studies have been attempted for glasses in the liquid state in contact with refractory compounds. The reaction kinetics of solution and reprecipitation during firing may establish concentration gradients in both the glass phase and the crystalline phase or phases and make such studies difficult to apply to real structures.

The control of microstructures in multiphase bodies of this type formed by sintering or hot pressing is difficult and often erratic. Further studies on the response of these complex systems to the forming process are necessary before controlled microstructures can be obtained.

Those materials of a refractory nature that can be melted and retained in the glassy state offer a novel approach to processing.[12] After forming a shape with the material in the glassy state by conventional glass working processes, a heat treatment is used to cause crystallization of the glass. The original glass composition contains compounds that act as nucleation sites and promote crystal growth during the final heat treatment. By proper control of these nucleation sites in the volume of the glass and the glass composition a glass, a glass-ceramic or a dense relatively glass-free ceramic may be produced all with an overall identical chemical composition. The unique microstructure produced by this process contains crystals as small as a few angstroms in size dispersed in a glass matrix or as small as a few hundred angstroms in size in the essentially completely crystallized state.

The analysis of the microstructure of ceramics produced by this method is complicated by 1) the small crystalline particle size, 2) the difficulty in determining the existence of residual glass, 3) the separation of surface nucleation and consequent surface microstructure from internal nucleation and produced internal microstructure, and 4) the chemical concentration gradients that possibly are introduced into the crystalline and glass phases during the crystallization process.

This process at present is limited in the number of compositions that are workable because of the temperature limits imposed by available materials for melting and forming glasses. It does offer new approaches to producing a controlled microstructure in refractory bodies and will probably make significant strides in this direction.

The metal bonded carbides have been studied extensively because of their technological importance in the tool bit industry. Their poor oxidation resistance and high density have limited their application to aerospace problems. The processing control especially with regard to the solubility of carbides in liquid metals and wetting characteristics of carbides by liquid metals[13] has advanced to the point where controlled microstructures can and are being produced by both sintering and hot pressing. Unfortunately, the relationship of the physical and chemical properties to the microstructure in these systems has not been pursued extensively as have the oxide multiphase or single-phase polycrystalline bodies. The evaluation of microstructural control in these systems is based on service performance and developed properties and not on laboratory tests on the processed material alone.

The refractories industry is an excellent example where controlled microstructures have been attained in multiphase refractory bodies.[14] In the development of basic refractories for open hearth roofs, the mineralogical constitution and distribution of phases have been optimized for performance in service. Contrary to the technical ceramics, the mechanical properties alone do not determine the attainment of a controlled microstructure. Characterization of the microstructure; laboratory tests on chemical composition, porosity, and room temperature and elevated temperature strength; and performance data are all combined to rate the specific refractory. The microstructure is then specified and used in process control. Further, changes in microstructure during service at elevated temperatures are used as guides for future developments. This interplay of processing, laboratory tests, and performance data has aided in the economical use of refractories in the steel industry.

Summary of the Control of Microstructure in Refractory Bodies

The drive to achieve high strengths through the production of a dense fine-grained polycrystalline refractory body has had a marked influence on the processing of ceramics. The unknown response of a specific material to the processing method is a major factor that has required each refractory compound to be studied individually. Knowledge of the densification mechanism and methods to control both normal grain growth and discontinuous grain growth in aluminum oxide have produced dense polycrystalline structures of moderate grain size. New processing techniques such as the controlled crystallization from a glass have achieved the desired grain size in an essentially glass-free ceramic, but the process is presently limited by the compositions that can be processed in this manner.

The control of the microstructure in these technical ceramics is dictated by the processing method employed. The fully characterized microstructure has not been attained, but increasing attention is being focused on details other than the grain size and density.

For those refractory materials where performance data in service are available, the microstructural analysis and control of the microstructure have advanced the technology significantly.

Model Microstructures

The refractory nature of the oxides, carbides, nitrides, borides, and beryllides has prompted investigations directed toward producing microstructures in lower melting compounds equivalent to those desired in the refractory materials. Scott and Pask[15] formed dense polycrystalline lithium fluoride specimens of high purity. The specimens were of large grain size. The forming method of melting and rapidly cooling limited the minimum grain size to about one-eighth of an inch. Although the microstructure could not be controlled to give smaller grain sizes, it was observed that the grain boundaries were not inherently weak.

The author in studying internal stresses[16] in ceramic systems proposed the use of glass-crystal bodies formed by vacuum hot pressing. In a dense multiphase system these bodies allow the best characterization of the microstructure attainable. The systems were formed by mixing powdered glass and powders of ceramic crystals in proportions to give the desired volume percent of crystals dispersed in a glassy matrix. By selecting ceramic crystals in a narrow size range, the particle size of the dispersed phase was controlled. Vacuum hot pressing of the mixture at temperatures where the glass phase just becomes fluid enough to flow under pressure minimized the tendency for bulk chemical reaction between the glass and crystal. Proper selection of the glass composition prevented crystallization of the glass phase and controlled the physical properties of the glass.

The multiphase systems formed by this technique could be characterized by knowledge of the following:

(1) The size, shape, and volume percent of crystalline material.

(2) The chemical purity and physical properties of the crystalline material.

(3) The volume percent of the glassy matrix phase.

(4) The chemical and physical properties of the glass phase.

The unknown quantities in the system and limitations were:

(1) The geometric arrangement of dispersed particles.

(2) The degree of interfacial bonding occurring between the glass and crystal.

(3) The availability of various crystal particle shapes in ranges from 0.1 to 100 microns in which each particle was a single crystal.

(4) For a single particle size of the crystalline phase, the limit on the amount of crystalline material that could be dispersed in the glassy matrix was approximately 50 volume percent. Above this amount porosity was introduced due to the packing arrangement of the crystals.

Jacobson[17] studied systems of the type described using nickel microspheres as the dispersed phase in a glassy matrix. Microscopic analysis of fracture surfaces indicated the lack of chemical bonding. Nason[18] in a recent study dispersed tungsten microspheres in glassy matrices and realized interfacial bonding. The fracture surface in this case was different from that of nickel in that the fracture appeared to propogate in the glass phase. In the nickel-glass bodies the fracture propogation was in the glass but tended to bisect the nickel spheres. The spheres would then pull cleanly away from the glass. This difference in fracture behavior based on interfacial bonding in model systems may be extended to polycrystalline single-phase materials through the use of vacuum hot pressed low melting crystalline matrices. Dispersed large particles relative to the matrix grain size may give information that will allow the interface to be characterized.

The use of model systems to achieve controlled microstructures has not appeared to be a profitable area because of the difficulty in predicting the response of a refractory system to processing methods. However, the use of model systems of controlled microstructure to extend our knowledge of the relation of properties to microstructure does appear feasible and should be pursued in the future.

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